

AD-A099 212

BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY

F/6 20/12

PREPARATION AND PROPERTIES OF THE SYSTEM $Fe(1-x)V(x)NbO_4$. (U)

MAY 81 B KHAZAI, R KERSHAW, K DWIGHT, A WOLD N00014-77-C-0387

UNCLASSIFIED

TR-16

NL

1 of 1
AD-A099 212

END
DATE
FILMED
6-81
DTIC

(14) TR-16

(12) Sc

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 16	2. GOVT ACCESSION NO. AD-A099212	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Preparation and Properties of the System Fe _{1-x} NbO ₄		5. TYPE OF REPORT & PERIOD COVERED (9) Technical rept.
7. AUTHOR(s) B. Khazai, R. Kershaw, K. Dwight and A. Wold		6. PERFORMING ORG. REPORT NUMBER 16
9. PERFORMING ORGANIZATION NAME AND ADDRESS Professor Aaron Wold Brown University, Department of Chemistry Providence, R. I. 02912		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0387
11. CONTROLLING OFFICE NAME AND ADDRESS Dr. David Nelson, Code 472 Office of Naval Research Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-359-653
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 22		12. REPORT DATE 15 May 1981
		13. NUMBER OF PAGES 22
		15. SECURITY CLASS. (of this report)
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted to the Journal of Solid State Chemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Vanadium Substituted Iron Niobate Wolframite Magnetic and Electrical Properties Phase Transformation		
ABSTRACT (Continue on reverse side if necessary and identify by block number) Members of the system Fe _{1-x} NbO ₄ were prepared and their crystallographic, electrical, and magnetic properties were determined. The wolframite structure is formed for x0.2, but for x0.4, a phase transformation to the rutile structure takes place. Magnetic studies established the formal valencies of the elements for members crystallizing with the wolframite phase. However, similar analyses of compounds with the rutile structure did not provide a unique assignment of the formal valencies.		

DTIC
ELECTE

MAY 21 1981

A

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

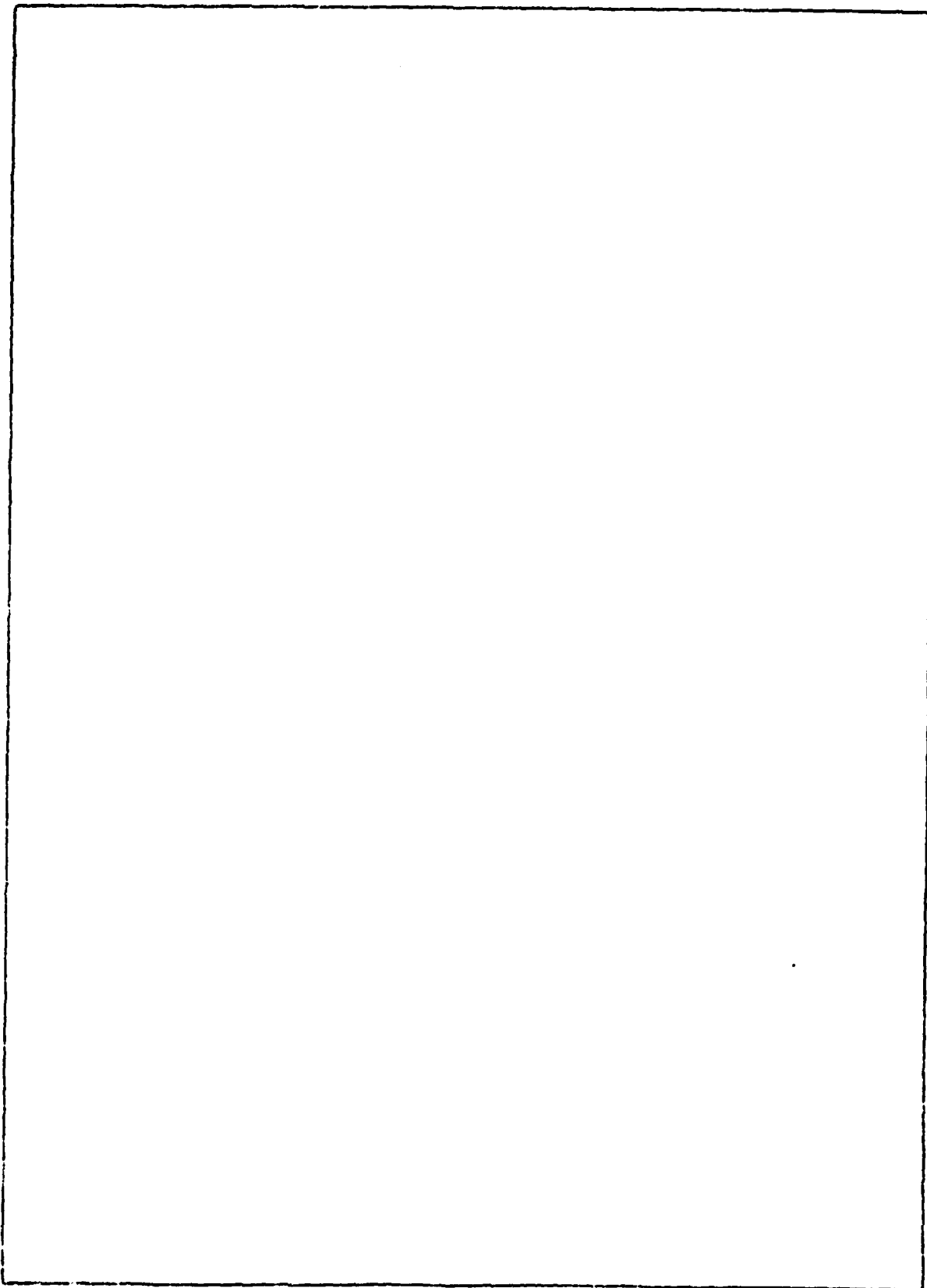
81 5 21 014

405436
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A099212

DTIC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)



SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0387

Task No. NR-359-653

TECHNICAL REPORT NO. 16

Preparation and Properties of the System $\text{Fe}_{1-x}\text{V}_x\text{NbO}_4$

by

B. Khazai, R. Kershaw, K. Dwight and A. Wold

Prepared for Publication

in the

Journal of Solid State Chemistry

Brown University

Department of Chemistry

Providence, Rhode Island

May 15, 1981

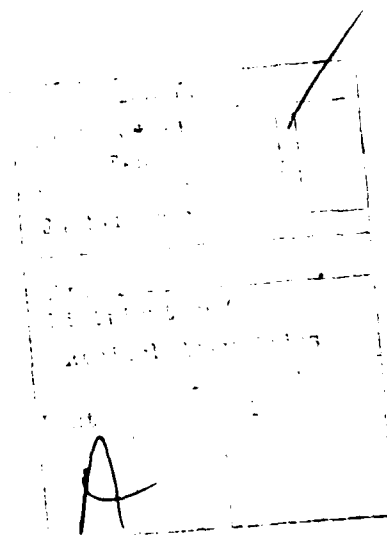
Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

INTRODUCTION

The substitution of ten atomic percent of chromium for iron in FeNbO_4 resulted in a significant lowering of the band gap (1). This is in good agreement with the reported decrease in the optical band gap of $\alpha\text{-Fe}_2\text{O}_3$ for a similar percent substitution of chromium (2). This observed lowering of the band gap was attributed to the formation of $\text{Cr}^{3+}(3d^3)$ energy levels within the optical band gap of FeNbO_4 .

Whereas in the system $\text{Fe}_{1-x}\text{Cr}_x\text{NbO}_4$, the only possible valence assignment for the transition metals was Cr^{3+} , Fe^{3+} and Nb^{5+} , the substitution of vanadium for iron in $\text{Fe}_{1-x}\text{V}_x\text{NbO}_4$ can give rise to multiple valence assignments. The measurement of the electrical and magnetic properties of a number of compositions in this system is useful in assigning appropriate valencies.



EXPERIMENTAL

Synthesis

All materials were prepared from the solid state reaction between Fe_2O_3 (Johnson-Matthey, spec pure), Nb_2O_5 (Kawecki Berylco Industries, spectroscopic grade) and V_2O_3 which was formed by the reduction of V_2O_5 (Johnson-Matthey) under a 15% hydrogen - 85% argon gas mixture. The vanadium-substituted iron niobate samples were made at 1000 °C in evacuated silica tubes to avoid any contact with air. Each product was x-rayed, ground, and reheated until a single phase was obtained. A Philips Norelco diffractometer, with $\text{CuK}\alpha$ radiation (1.5405\AA) at a scan rate of $0.25^\circ 2\theta \text{ min}^{-1}$, was used to carry out the x-ray analysis.

Discs were formed by pressing aliquots of approximately 150 mg at 90,000 p.s.i.; the pressed discs were placed in a sealed silica tube and heated at a rate of 85 °C per hour to 1000 °C, and maintained at that temperature for 24 hours. After the sintering process, the discs were cooled at the same rate.

X-ray diffraction patterns of the sintered discs showed, at the limit of detection, the presence of the strongest line of $\alpha\text{-Fe}_2\text{O}_3$, which is consistent with the formation of a solid solution of FeNb_2O_6 in FeNbO_4 under the sintering conditions. Essentially identical resistivities were measured before and after abrading these discs to one half their original thickness, which established their homogeneity.

Magnetic Measurements

Magnetic susceptibilities were measured using a Faraday balance (3) over the range from liquid nitrogen to room temperature at a field strength of 10.4kOe. Honda-Owen (field dependency) plots were also made to determine the presence or absence of ferromagnetic impurities. The data were then corrected for core diamagnetism (4).

Electrical Measurements

The resistivities of the samples were measured using the Van der Pauw technique (5). Contacts were made by the ultrasonic soldering of indium directly onto the samples, and their ohmic behavior was established by measuring their current-voltage characteristics.

RESULTS AND DISCUSSION

The influence of $V^{3+}(3d^2)$ on the phase transition of $FeNbO_4$ bears a striking resemblance to that of $Cr^{3+}(3d^3)$ (1). The system $Fe_{1-x}V_xNbO_4$ forms a solid solution over the range of $0 \leq x \leq 0.2$ which crystallizes with the wolframite $FeNbO_4$ structure (space group $P2_1/C$) shown in figure 2. At values of $x \geq 0.4$, a phase transformation to the rutile structure (space group $P4_2/mnm$) shown in figure 2 takes place. The crystallographic data for this system are summarized in Table I. However, in contrast to the chromium-substituted system, the electrical and magnetic behavior cannot be explained in terms of a simple localized model.

The results of the magnetic measurements are summarized in Table II. In the region $0 \leq x \leq 0.2$, the compounds show a Curie-Weiss behavior. The experimental Curie constants of 3.70 and 3.06 for the compositions $x=0.1$ and $x=0.2$ (wolframite structure) can only be accounted for if an assignment of $V^{4+}(3d^1)$ is made for the formal valence of vanadium. An equivalent amount of $Fe^{2+}(3d^6)$ is assumed for the formal valence of iron, with the remainder of the iron present as $Fe^{3+}(3d^5)$. Hence, the formula for the wolframite members may be represented by $Fe^{3+}_{1-2x}Fe^{2+}_xV^{4+}_xNb^{5+}_xO_4$. The resistivity values reported for sintered discs of compositions having this structure indicate that these phases show considerable conductivity. It can be seen from an examination of the wolframite structure (figure 1) that one half of the zig-zag

chains along the c direction contain Nb^{5+} , whereas the other chains have Fe^{2+} , Fe^{3+} , as well as V^{4+} . Conductivity undoubtedly results from the mixed valence states present in these chains.

The magnetic properties of the members of the system crystallizing with the rutile structure indicate more complex behavior. VNbO_4 , itself, shows Curie-Weiss behavior (figure 3). Its Curie constant of 1.1 given in Table II is consistent with d^2 vanadium (V^{3+}), and there is no apparent contribution from Nb^{5+} ($\mu_{\text{eff}} = 0$). However, for other members of the vanadium-substituted system crystallizing with the rutile structure ($0.4 \leq x \leq 1$), deviations from Curie-Weiss behavior are observed which increase with decreasing values of x. The marked deviation shown in figure 3 for $x=0.4$ precludes the evaluation of a reliable Curie constant. Results of field dependency shown in figure 4 indicate the existence of a ferromagnetic component for $x=0.4$. Hence, the susceptibility data cannot be used reliably for the assignment of formal valencies for members of the system $\text{Fe}_{1-x}\text{V}_x\text{NbO}_4$ crystallizing with the rutile structure.

Rüdorff and Märklin (6) have reported, and Villeneuve et al (7) have confirmed that for the system $\text{V}_{1-x}\text{Nb}_x\text{O}_2$, the electrical resistivity increases with increased niobium concentration. Rüdorff indicated that the rutile phase was composed of two mixed oxide phases $(\text{V}^{4+}_{1-x}\text{V}^{3+}_x\text{Nb}^{5+}_x)\text{O}_2$ with $0 < x < 0.5$, and $(\text{V}^{3+}_{1-x}\text{Nb}^{5+}_{1-x}\text{Nb}^{4+}_{2x-1})\text{O}_2$ with $0.5 < x < 1.0$. In addition, for $\text{V}^{3+}\text{Nb}^{5+}\text{O}_4$, the resistivity was a maximum. The presence of two valence states for either the niobium or vanadium was responsible for the higher conductivity of the other members of the system.

Similarly, in this study, electrical and magnetic measurements obtained on the end member VNbO_4 support the presence of V^{3+} , Nb^{5+} . However, the introduction of iron results in the formation of mixed valencies of vanadium and, possibly, also niobium. This would be consistent with the relatively high conductivity values given in Table II for the rutile members of the series; since otherwise, a random occupation of 50% of the cation sites by Nb^{5+} would block any possible conductivity.

These considerations, together with the complex magnetic behavior observed for the composition $x=0.4$, preclude any attempt to assign formal valencies.

TABLE I

Precision Lattice Constants for the System $\text{Fe}_{1-x}\text{V}_x\text{NbO}_4$

	<u>a(Å)</u>	<u>b(Å)</u>	<u>c(Å)</u>	<u>β(deg.)</u>
FeNbO_4	4.997(2)	5.619(2)	4.651(2)	90
$\text{Fe}_{.9}\text{V}_{.1}\text{NbO}_4$	4.998(2)	5.613(2)	4.646(2)	90
$\text{Fe}_{.8}\text{V}_{.2}\text{NbO}_4$	5.007(2)	5.613(2)	4.646(2)	89.87
$\text{Fe}_{.6}\text{V}_{.4}\text{NbO}_4$	4.685(2)	-	3.037(2)	-
$\text{Fe}_{.4}\text{V}_{.6}\text{NbO}_4$	4.684(2)	-	3.034(2)	-
VNbO_4	4.677(2)	-	3.034(2)	-

TABLE II

Electrical and Magnetic Data for the System $\text{Fe}_{1-x}\text{V}_x\text{NbO}_4$

	Structure ^(a)	ρ (Ω -cm)	C_M expt'l	C_M theo ^(b)	Formal Valence Assignment
FeNbO_4	W	40(1)	4.18	4.35	$\text{Fe}^{3+}, \text{Nb}^{5+}$
$\text{Fe}_{.9}\text{V}_{.1}\text{NbO}_4$	W	84(1)	3.70	3.68	$\text{Fe}^{3+}_{.8}, \text{Fe}^{2+}_{.1}, \text{V}^{4+}_{.1}$
$\text{Fe}_{.8}\text{V}_{.2}\text{NbO}_4$	W	115(2)	3.06	3.17	$\text{Fe}^{3+}_{.6}, \text{Fe}^{2+}_{.2}, \text{V}^{4+}_{.2}$
$\text{Fe}_{.6}\text{V}_{.4}\text{NbO}_4$	R	1520(11)	-	-	-
$\text{Fe}_{.4}\text{V}_{.6}\text{NbO}_4$	R	1900(29)	-	-	-
VNbO_4	R	$>10^4$	1.10	1.0	$\text{V}^{3+}, \text{Nb}^{5+}$

(a) W = Wolframite R = Rutile

(B) Corrected for $C_M(\text{Fe}^{3+}) = 4.18$

ACKNOWLEDGMENTS

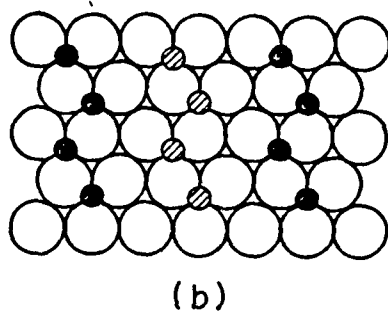
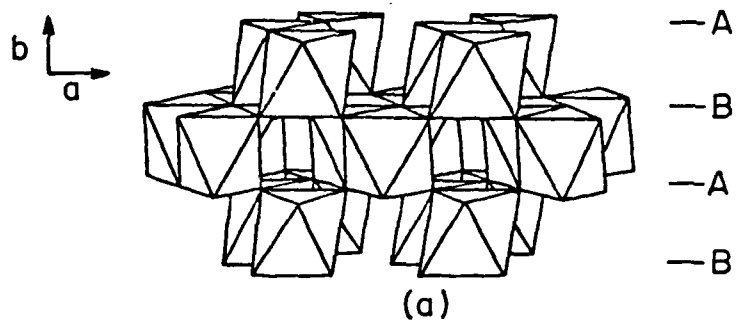
The Office of Naval Research, Arlington, Virginia, supported the work of Bijan Khazai and Kirby Dwight. In addition, the authors would like to acknowledge the support of the Materials Research Laboratory Program at Brown University.

REFERENCES

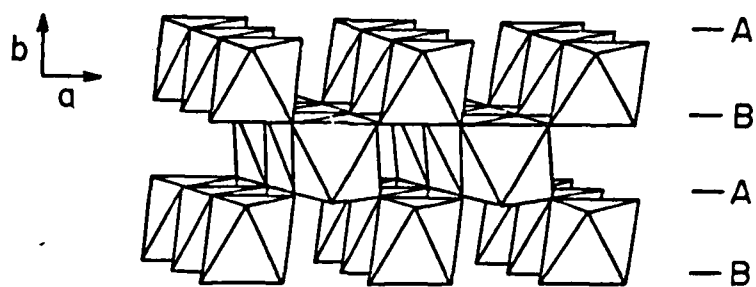
1. B. Khazai, R. Kershaw, K. Dwight and A. Wold, Submitted to Journal of Solid State Chemistry.
2. P. Merchant, R. Collins, R. Kershaw, K. Dwight and A. Wold, J. Solid State Chem. 27, 307 (1979).
3. B. Morris and A. Wold, Rev. Sci. Inst. 39, 1937 (1968).
4. P. W. Selwood, "Magnetochemistry" 2nd ed., Interscience Pub. Co. (1956).
5. L. J. Van der Pauw, Philips Res. Rep. 13, 1 (1958).
6. V. W. Rüdorff and J. Märklin, Z. Anorg. Allg. Chem. 334, 142 (1964).
7. G. Villeneuve, A. Bordet, A. Casalot, J. P. Pouget, H. Launois and P. Lederer, J. Phys. Chem. Solids 33, 1953 (1972).

FIGURE CAPTIONS

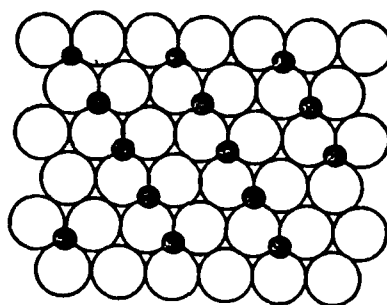
- Figure 1 Structure of FeNbO_4 : (a) packing of MO_6 octahedra;
 (b) closest-packed layer of oxygen around Fe and
 Nb atoms.
- Figure 2 Structure of rutile: (a) packing of MO_6 octahedra;
 (b) closest-packed layer of oxygen around V and
 Nb atoms.
- Figure 3 Thermal variation of the inverse magnetic suscepti-
 bility for VNbO_4 and $\text{Fe}_{.6}\text{V}_{.4}\text{NbO}_4$.
- Figure 4 Variation of χ_{eff} with inverse applied field for
 $\text{Fe}_{.6}\text{V}_{.4}\text{NbO}_4$ at 77 K and 300 K.



● Fe ▨ Nb

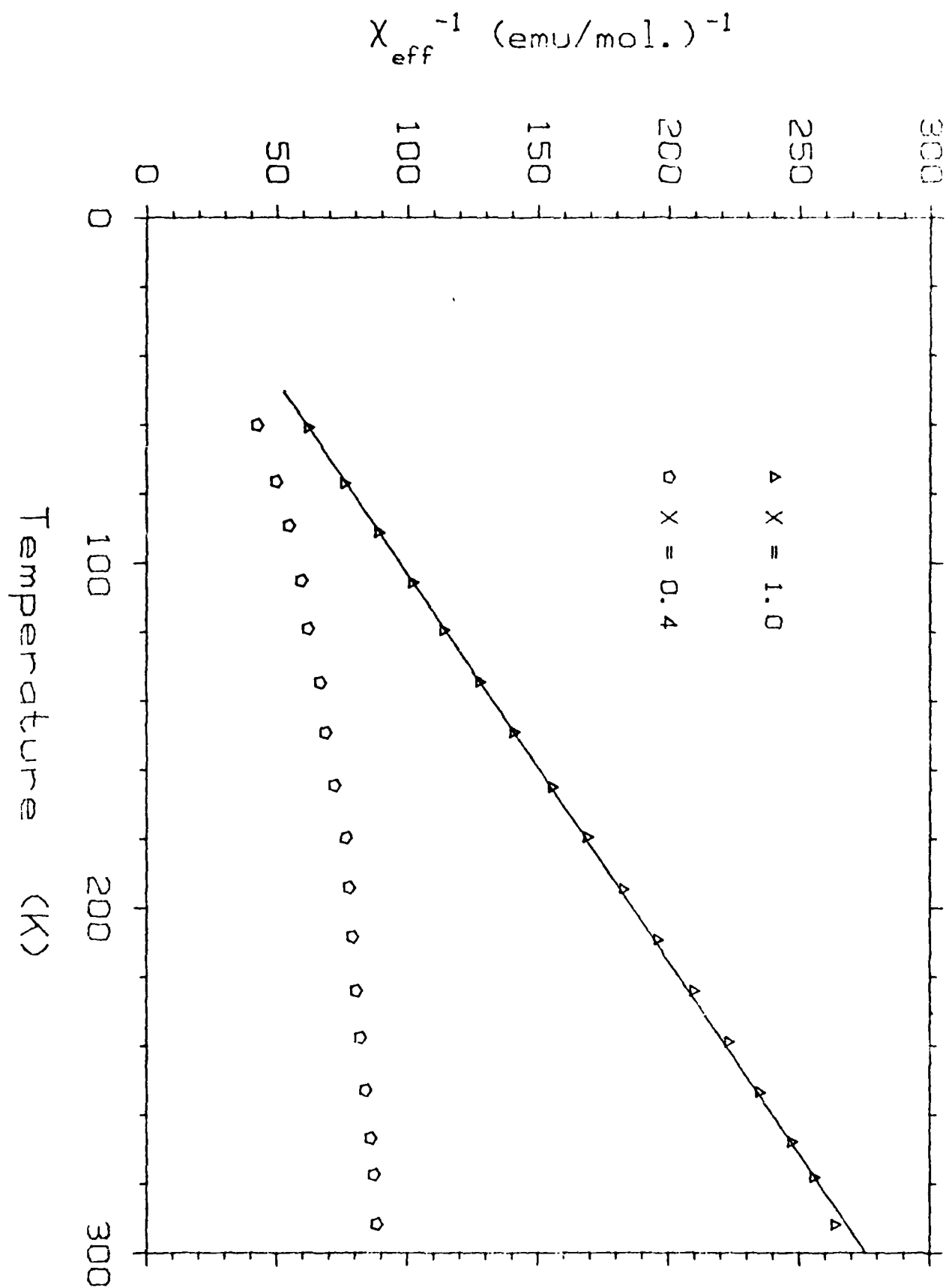
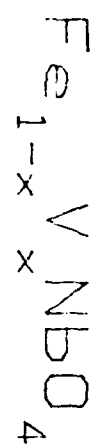


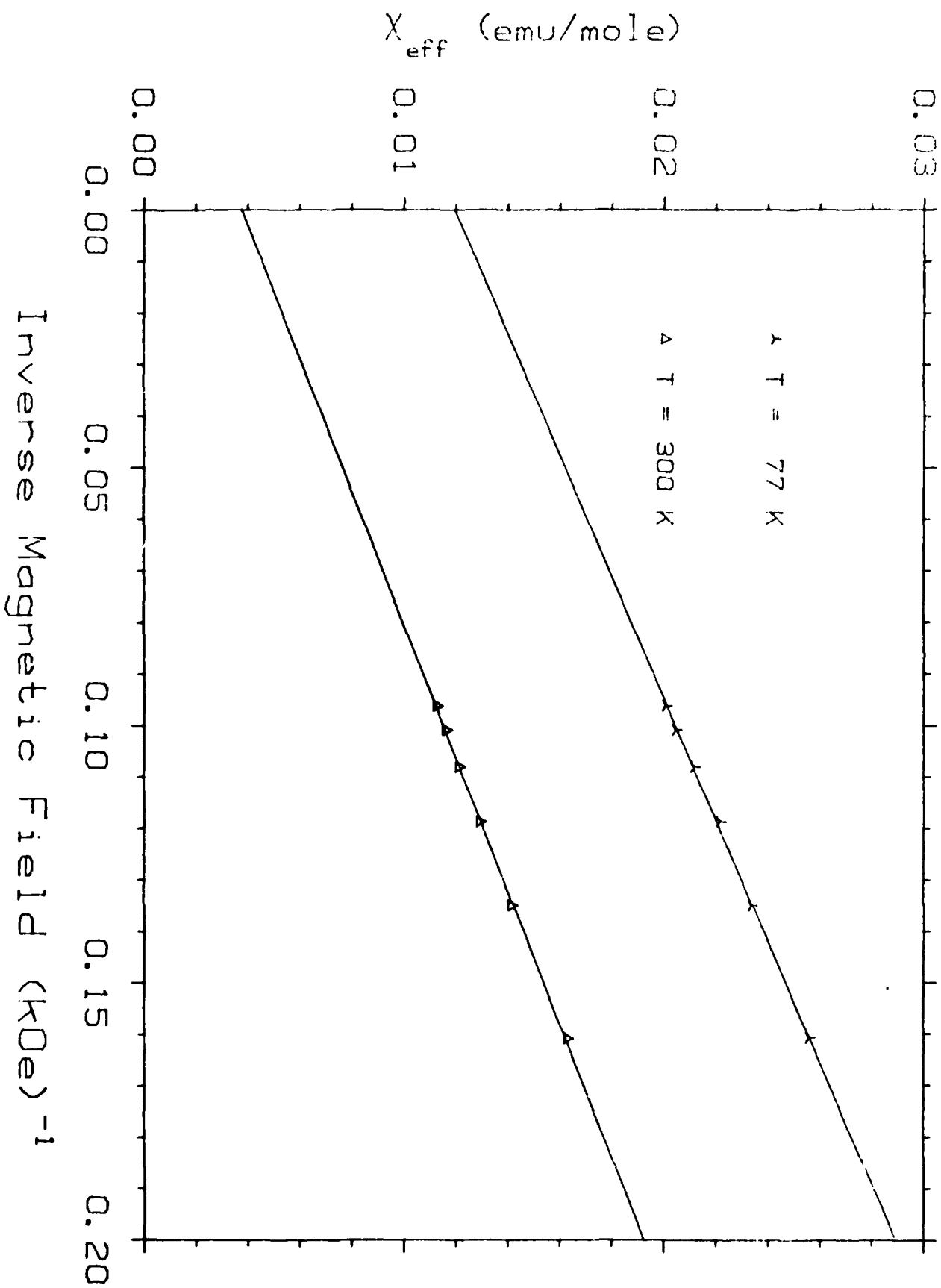
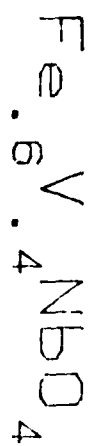
(a)



(b)

● V/Nb





TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
		Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Paul Delahav Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southhampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co., Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer FIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. W. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6C 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Rubv DOF (STOR) 600 F Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SO9 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Ostervoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1		
Dr. A. Himv NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

END

DATE
FILMED

6 - 8 - 1

DTIC